able to form oxide and silicate condensates at higher temperatures than in a fully speciated solar gas, in which the SiO molecule stabilizes Si in the vapor phase. In the present case, the free Si combines with the free O to condense cristobalite (SiO_2) at 1860 K, a higher temperature than that for any other refractory oxide, and after 99.6% of the C has already condensed as graphite. At 1820, Ti_4O_7 condenses and is replaced by TiO_2 at 1790 K, where mullite ($Al_6Si_2O_{13}$) also appears. Anorthite ($CaAl_2Si_2O_8$) appears at 1770 K, and mullite disappears at 1750 K. Sphene ($CaTiSiO_5$) replaces TiO_2 at 1700 K, wollastonite ($CaSiO_3$) appears at 1680 K, and whitlockite ($Ca_3(PO_4)_2$) appears at 1610 K. Wollastonite is replaced by diopsidic pyroxene ($CaMgSi_2O_6$) at 1590 K. Cristobalite disappears at 1530 K, just before forsteritic olivine (Mg_2SiO_4) finally appears at 1520 K. In a solar gas composed entirely of monatomic species, at 10^{-6} bar total pressure, graphite and cristobalite are the most abundant condensates between 2100 K and 1600 K.

Suppression of the polyatomic molecular species in a solar gas at 10^{-6} bar total pressure changes the order of major-element condensation from Al-Ca-Ti-Si-Mg to C-Si-Ti-Al-Ca-Mg. The mechanism called upon by Clayton [3] is unlikely to yield SiC or TiC grains, even if grains could nucleate in an environment that destroys gaseous molecules. Our calculations suggest that, instead of SiC and TiC, SiO_2 would co-condense with graphite. One might expect extrasolar graphite to be accompanied by extrasolar SiO_2, if graphite did indeed form in the manner Clayton [3] suggests. Inclusions of SiO_2 have not been discovered in searches of extrasolar graphite.

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CHEMICAL COMPOSITION OF MARTIAN METEORITES. M. Ebihara[1], K. Shinotsuka[2], and P. Kong[3], [1]Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan (ebihara-mitsuru@c.metro-u.ac.jp), [2]National Institute for Fusion Science, Gifu 509-5292, Japan, [3]Mineralogical Institute, Universität zu Köln, 50674 Köln, Germany.

We have analyzed three shergottites (ALH 77005, EET 79001, and Zagami), one orthopyroxenite (ALH 84001) and one nakhalite (Nakhla) by instrumental neutron activation analysis (INAA) for major, minor, and trace elements, radiochemical neutron activation analysis (RNAA) for siderophiles, and inductively coupled plasma mass spectrometry (ICP-MS) for REE, Th, and U. Our INAA data generally agree with the literature values for individual meteorites [1–3]. In spite of a large variety of petrological types, the constancy in Fe and especially Mn is remarkable. Very close coherence of Mn with Fe due to the similarity in ionic radius of Fe^{2+} and Mn^{2+} is obvious for martian materials, as was observed for the terrestrial and lunar rocks.

In contrast to Co, which is another element not variable among the six martian meteorites analyzed, Ni is highly depleted in ALH 84001. In fact, ALH 84001 is notably depleted in refractory siderophile elements such as Ir and Os compared to other martian meteorites. Lherzolitic shergottites have a Ir/Os ratio very close to the CI chondrite ratio [4]. This is also true for EET 79001, but Zagami has 2× CI ratio of Ir/Os. Nakhla has an even higher Ir/Os ratio (relative CI ratio) than four shergottites, while ALH 84001 has a much lower Ir/Os ratio than CI ratio. A large depletion of siderophile elements in ALH 84001 coupled with its very old formation age (4.5 Ga) suggest that the core formation took place at an early stage of martian history.

The chondrite-normalized REE abundance pattern of lherzolitic martian meteorites is characterized by the presence of a hump in the middle to heavy REE span. Whereas the abundance increases in the light REE span, the abundance decreases in the heavy REE span. Similar patterns are observed for EET 79001 and Zagami in this study. In addition to the hump in the middle REE region, a slight increase from Ce to La is commonly observed for shergottites including lherzolitic shergottites. This upward curvature at the lightest REE may required the third component of REE carrier in shergottites. The REE abundance pattern for ALH 84001 is completely different from those for shergottites; REE pattern is flat in light REE and is gradually and monotonously increased toward heavy REE. This pattern suggests that at 4.5 Ga, the partial or extensive melting occurred on Mars, with the melt being segregated from the mantle or cumulates, from which ALH 84001 was formed.

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GEOCHEMISTRY OF CARBONATES AND GLASS IN ALLAN HILLS 84001. J. M. Eiler[1], J. W. Valley[2], C. M. Graham[3], and J. Fournelle[2], [1]Geological and Planetary Sciences, California Institue of Technology, Pasadena CA 91125, USA (eiler@gps.caltech.edu), [2]Geology and Geophysics, University of Wisconsin, Madison WI 53706, USA, [3]Geology and Geophysics, University of Edinburgh, Edinburgh Scotland, UK.

The stable isotopic geochemistry of carbonates in SNC meteorites constrains both the characteristics of martian volatile reservoirs and the origin of secondary mineralization in these samples. We here report new ion microprobe measurements of $^{18}O/^{16}O$ in carbonates and related phases in ALH 84001, supported with major-, minor-, and trace-element data on the same materials.

The background for these measurements is that carbonates in ALH 84001 display a large range in O-isotopic composition (~25‰; [1–4]), which has been ascribed either to variations in temperature [1,3,5] or Rayleigh distillation [4]. When examined in detail, variations in the O-isotopic ratio in carbonates have been shown to be correlated systematically with variations in their major-element composition [1,3,4]. Although the data from several different groups are generally consistent, one difference is that ankeritic carbonates (~50% $CaCO_3$) were reported by [3] to have $\delta^{18}O_{SMOW}$ Å 0‰, but [4] found values of ~7‰ for carbonates in this compositional range.

We made 82 measurements of $\delta^{18}O$ in carbonates from ALH 84001, including a range of ankeritic compositions not encountered in previous studies and ~20 measurements each of all of the major populations/textural types of carbonate known in this sample. Our results confirm the overall trend of $\delta^{18}O$ with chemical composition seen in previous studies [1–4]: i.e., $\delta^{18}O$ varies by ~25‰ and tends to decrease with increasing Ca content. However, our data reveal details in the correlations between $\delta^{18}O$ and chemistry not observed in previous, smaller data sets. In particular, two distinct, offset trends occur in plots of $\delta^{18}O$ vs. major elements: (1) decreasing $\delta^{18}O$ (26 → 0‰) with decreasing Mg and increasing Ca and Mn in white magnesites and orange magnesio-siderites, and (2) ankerites having a large range in chemical composition ($0.45 \le X_{Ca} \le 0.71$) with essentially indistinguishable $\delta^{18}O$ values (5.8 ± 1.9‰). There may be a subtle discontinuity in $\delta^{18}O$ and chemical composition on the first trend, between magnesites ($0.70 \le X_{Mg} \le 0.90$; $X_{Ca} \le 0.05$) and magnesio-siderites ($X_{mg} < 0.70$; $0.08 \le X_{Ca} \le 0.44$). Our results for ankeritic carbonates are within analytical uncertainty of [4] and in disagreement with [3]. These two trends are associated with distinct carbonate textures: magnesites and magnesio-siderites are found principally in concentrically zoned "disks" [6] and ankerites are found exclusively in irregularly shaped patches.

Manganese concentration is strongly correlated with Ca in ALH 84001 carbonates. There are again two distinct trends, one for magnesites and magnesio-siderites and one for ankeritic carbonates, offset from each other in Ca/Mn ratio. On average, the ankerites also have higher La/Nd and Sr/Ba ratios, higher Sr and Y concentrations, and lower Ba concentrations than magnesites and magnesio-siderites. $\delta^{18}O$ is negatively correlated with La/Nd and Sr/Ba among all analyses. On average, magnesites have higher La/Y ratios and Th concentrations than other carbonate populations. All populations of carbonate have LREE-depleted REE patterns relative to coexisting feldspathic glass [see also 7].

Differences in REE abundances between carbonates and feldspathic glasses are not those predicted by carbonate/silicate-melt distribution

coefficients, and therefore no population of carbonate considered in this study can be consanguineous with melt from which much of the glass in ALH 84001 appears to have quenched. Rare-earth-element and other trace-element abundances vary systematically with crystallization sequence (e.g., decreasing La/Nd from ankerite → magnesio-siderite → magnesite). These variations are in the opposite direction of those predicted by fractional precipitation from a carbonic fluid based on known carbonate/fluid distribution coefficients. Given correlations between $\delta^{18}O$ and chemistry, models in which variation in $\delta^{18}O$ is due to precipitation over a range of temperatures require complex variation of fluid/carbonate distribution coefficients with temperature. Alternatively, carbonate may have precipitated from at least two chemically and isotopically distinct fluids, such that correlations among $\delta^{18}O$ and chemistry reflect different mixing proportions of endmember fluid compositions.

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A NEW POSTSTISHOVITE SILICON DIOXIDE POLYMORPH WITH THE BADDELYITE STRUCTURE (ZIRCONIUM OXIDE) IN THE SNC METEORITE SHERGOTTY: EVIDENCE FOR EXTREME SHOCK PRESSURE.

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Shergotty contains silica grains with lamellar structures that were interpreted to be shock-induced PDFs in quartz [1]. Consequently, an "equilibrium peak-shock pressure" of 29 ± 1 GPa was estimated [1]. Detailed scanning electron microscopy and transmission electron microscopy investigations of the silica in Shergotty demonstrated that the lamellar microstructure is not a result of pressure-induced amorphization, i.e., PDFs, but constitutes an intergrowth of very high-density post-stishovite SiO_2 and SiO_2 glass formed by the vitrification of the high-pressure polymorph after pressure release [2,3]. This new silica polymorph has an α-PbO_2-like structure, possibly between α-PbO_2 and SBAD [2,3]. Based on electron diffraction, the structure appears to be the same as a very dense polymorph produced in shock experiments at pressures between 70 and 90 GPa [4]. This new dense post-stishovite phase can be used as an indicator of extreme shock pressures in terrestrial and extraterrestrial samples.

Recent high-pressure diamond-anvil experiments and molecular dynamics simulation calculations revealed that SiO_2 undergoes several phase transitions from stishovite to denser polymorphs above 45 GPa [5–8]. These polymorphs are $CaCl_2$ structured above 45 GPa, and α-PbO_2 structured (Pbcn) and modified baddeleyite structured (Pnc2; SBAD) above 80 GPa [7–9]. The last three polymorphs should be stable above 85 GPa [5–7]. Teter et al. [7] suggest that there are thousands of competitive polymorphs of silica with similar total energy above 80 GPa [7]. Hence, the α-PbO_2-like SiO_2 structure found in Shergotty [2,3] may be one of several post-stishovite polymorphs of silica in Shergotty. Shergotty is therefore an ideal meteorite in which to search for additional post-sishovite SiO_2 species, to scrutinize the possible stable structures among the post-stishovite SiO_2 polymorphs. Furthermore, additional post-stishovite SiO_2 polymorphs in Shergotty may provide new constraints on peak-shock pressures.

We surveyed the microstructures of more than 30 silica grains. There are large variations in the intergrowth textures among the silica grains. Each grain consists of hundreds of coherent domains 10–60 μm in diameter. However, not all domains display the orthogonal lamellar structure found in the α-PbO_2-bearing grains [2,3]. Some domains display no lamellae. The laminar and nonlamellar domains have the same chemical compositions [2,3]. We selected a grain with several nonlamellar domains for X-ray diffraction studies and TEM investigations.

TABLE 1. d-spacings (in Å) and indexes of X-ray reflections of the new very dense baddeleyite-structured SiO_2 polymorph of silica in Shergotty.

d-obs	d-calc	I-obs	I-calc	hkl
4.309	4.3087	10	7	100
3.260	3.2587	22	27	001
3.139	3.1394	6	11	110
2.974	2.9146*	7		
2.767	2.7667	100	100	$11\bar{1}$
2.639†		10		
2.459	2.4595	31	35	111
2.318	2.3183	11	9	002
2.207	2.2073	8	3	$10\bar{2}$
2.023	2.0234	14	2	120
1.950	1.9497	26	11	210
1.913	1.9125	4	14	121
1.762	1.7617	12	21	112
1.629	1.6299	24	27	022
1.591	1.5898	19	25	$12\bar{2}$
1.568	1.5697	18	31	220
1.458	1.4573	16	14	202
1.355	1.3532	8	13	131

Cell parameters: a = 4.375 Å; b = 4.584 Å; c = 4.708 Å; β = 99.97. Space group: baddeleyite ($P2_1/c$).

* Could be due to a small amount of stishovite.

† Could be due to α-PbO_2 (Pbcn) polymorph.

The X-ray diffraction pattern consisted of 18 reflections (Table 1). This pattern could not be indexed as any of the low-pressure polymorphsof silica, or the high-pressure polymorphs coesite, stishovite, $CaCl_2$-, α-PbO_2-structured, or SBAD [5–7]. Overall, the diffraction data cannot be fit by the α-PbO_2-like polymorph of German et al. [4]. All reflections (except one at d = 2.639 Å) could be indexed in terms of a monoclinic cell (Table 1). These parameters are identical to the calculated values for the baddeleyite (ZrO_2)-structured (space group $P2_1/c$) polymorph of silica (Table 1). The reflections with d-spacings 2.63Å and 3.26 Å also match the electron diffraction data previously measured in Shergotty [3]. The agreement between the measured and calculated d-spacings and the intensities of the individual reflections is excellent (Table 1). The calculated density of this high-pressure polymorph of silica is r = 4.30 (2) g/cm^3. This is slightly higher than the densities of both stishovite (4.28 g/cm^3) and the α-PbO_2-structured polymorph (4.29 g/cm^3). This is the first natural occurrence of a very dense silica polymorph with seven-coordinated silicon.

Calculations [5] reveal that the SiO_6 octhedra of the SBAD will be distorted and transformed to seven-apex polyhedra (characteristic of baddeleyite) during pressure decrease to 10 GPa. Experiments in the diamond-anvil cell at P > 85 GPa and 2000 K produced the SBAD polymorph [6]. We anticipate that the ZrO_2-structured polymorph formed from a parental SBAD phase upon decompression from a shock-state higher than 85 GPa. The presence of both the α-PbO_2-like and ZrO_2-structured SiO_2 polymorphs in the same meteorite and possibly in the same parental silica grains is a strong hint to the predicted presence of numerous structures at high pressures [7]. We have not encountered silica grains with the ideal α-PbO_2 structure in Shergotty so far.

The present finding provides additional evidence that the peak-shock pressures experienced by Shergotty were in excess of 85 GPa, perhaps close to 90 GPa.

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